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Physico-Chemical Disintegration of Concrete

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The purpose of this paper is to list and discuss briefly some of the causes of chemical and physico-chemical disintegration of concrete and to point out some methods that can be used to study these causes.

In this paper a distinction is made between physico-chemical (or chemico-physical) and mechanical causes of failure. Processes involving changes in chemical composition (chemical reactions proper), changes in phase of a component (freezing of water and crystallizing of salts in voids), capillary forces, and temperature stresses are considered to be physico-chemical; processes involving stress from the surrounding environment (traffic loads, uneven swelling of supporting medium, etc.) are considered to be mechanical.

As concrete making and study have been evolving from an art to a science, more and more attention has been placed on so-called fundamental study of chemical and physical processes in concrete. However, so many variables are involved, and so few organizations are (or consider themselves to be) vitally involved financially, that research on concrete has lagged. On the other hand, in the highly organized cement industry fundamental work on the nature and properties of cement has been in progress for many years. At the present time there is a tremendous upsurge of interest in the chemistry and physics of concrete, as evidenced by a voluminous literature. Engineers are realizing that chemical and physical processes of disintegration are responsible for a large portion of concrete failures.

TYPES OF AND METHODS FOR STUDY OF PHYSICO-CHEMICAL DISINTEGRATION OF CONCRETE

Alkali-Aggregate Reaction

In 1940 Stanton pointed out and emphasized the importance of this phenomenon. After considerable debate and doubting, most concrete research men have come to accept the reality of such a reaction. Large-

scale studies have been made and are under way to prevent occurrence of this reaction and to determine its mechanism. Reportedly a very large mileage of pavement as well as several dams has been damaged or destroyed by alkali-aggregate reaction.

The mechanism of the reaction is somewhat as follows: Certain mineral constituents of aggregates—primarily opal—react with sodium and potassium hydroxide—derived from the cement—to form alkali silicates. The cement mortar acts as a semi-permeable membrane, holding the large molecules of alkali silicate (sometimes in solution and sometimes a gel-like mass) at the point of formation, but permitting migration of water from other regions to that point. The alkali silicate imbibes water by an osmotic process, and a pressure is generated as more and more water attempts to enter the pocket or area holding the alkali silicate. Calcium ions may replace the sodium and potassium in the reaction product, thus permitting them to react with more aggregate.

Several methods for detection of reaction or potential reaction of cement-aggregate combinations are available. Chemical analysis of the cement will show the amount of alkali present. There is a trend to make an empirical division of 0.5% sodium oxide equivalent (percentage sodium oxide plus 0.658 times the percentage potassium oxide) between "high" and "low" alkali cements and thus, presumably, a division between potentially "reactive" and "non-reactive" cements. There is also considerable disagreement with this line of reasoning.

Chemical analysis of aggregates will furnish information concerning elemental composition but not usually concerning molecular composition. However, methods of calculation are available for converting results of chemical analysis to mineralogical composition. Chemical analysis is frequently called for in a great variety of specialized problems in study of concrete, which can be determined only after the study is in progress.

Petrographic (and even macroscopic) examination of aggregate will show the presence or absence of minerals which tend to expand when used in combination with certain cements.

The bomb test, developed at the Denver laboratory of the Bureau of Reclamation, measures alkali reactivity of aggregates by measuring the amount of silica dissolved and the reduction in alkalinity when a powdered sample of aggregate is exposed to a one-normal solution of sodium hydroxide in a sealed container for 24 hours at 80°C.

The results of the test are plotted on a graph as amount of silica dissolved against reduction of alkalinity. An empirically-derived curve, separating reactive from non-reactive aggregates, has been drawn on

this graph. Of the large number of Indiana aggregates tested, all were far over in the non-reactive area except samples from the Liston Creek formations (high silica), which were just within the non-reactive area. Figure 1 shows these results.

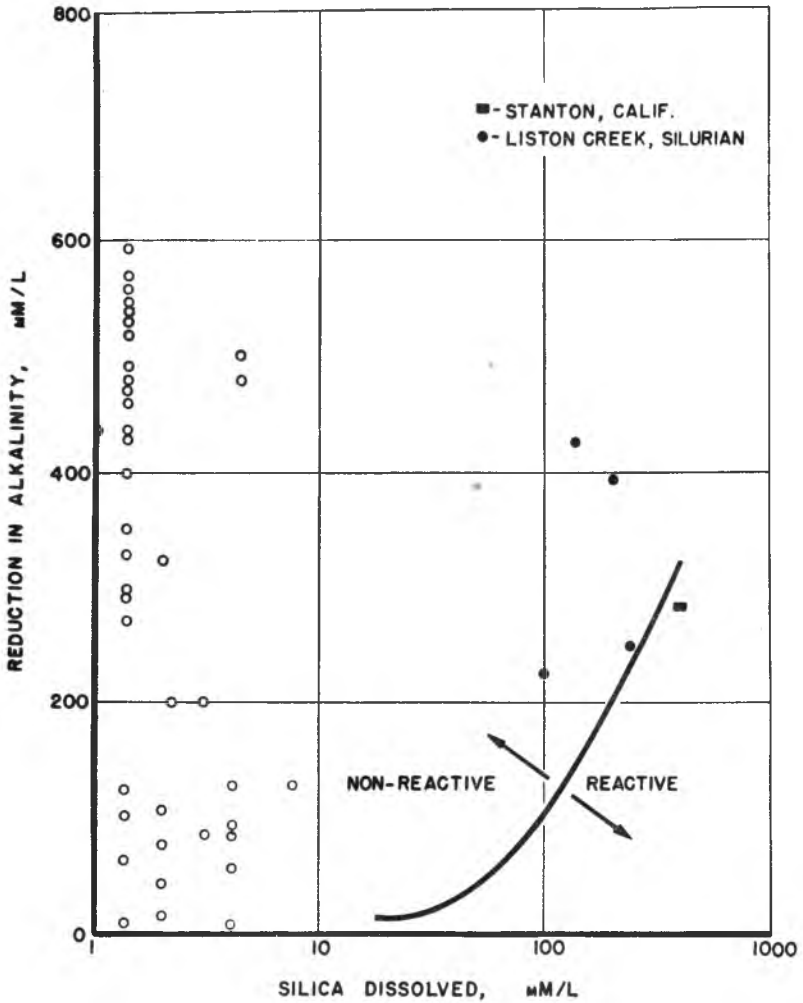

FIGURE 1. Results of alkali-reactivity bomb test on Indiana aggregates.

Other tests involved study of combinations of cement and aggregate, rather than study of each separately. The mortar-bar expansion test is perhaps the most popular. Mortar bars (usually one-by-one-by-ten inches) containing the combination of cement and aggregate in

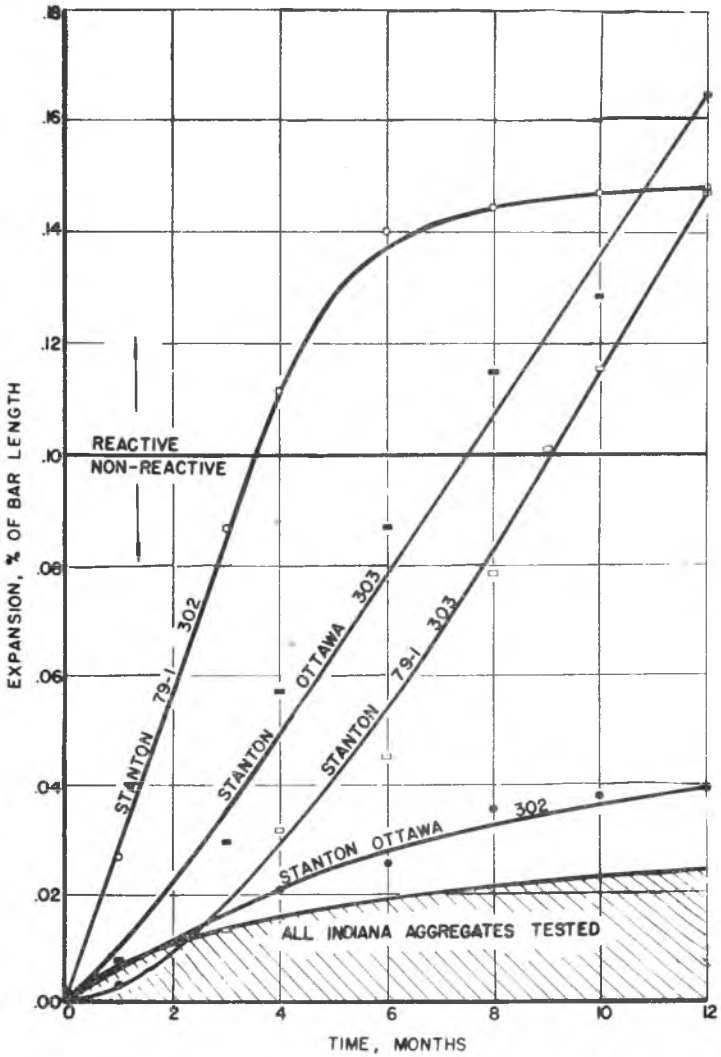

FIGURE 2. Results of expansion-bar test on Indiana aggregates.

question (usually the aggregate being studied is used in amount of five or ten percent of total aggregate, the remainder being an "inert" aggregate filler) are stored at constant temperature in an atmosphere of 100-percent relative humidity and measured periodically for changes in length. A percentage of linear expansion of over 0.1 percent within six months is generally considered to indicate reactive combinations. A series of such tests was run on Indiana limestones, cherts, and gravels;

not one of these aggregates was indicated as reactive, as shown by Figure 2.

The pat test is used as an indication of reactivity or non-reactivity of cement-aggregate combinations. This test involves storage of mortar specimens under a solution 0.5 normal each in sodium and potassium hydroxide. The mortar contains pieces of aggregate about one-fourth inch across; the mortar specimens (usually two-inch cubes) are sawed in half to present a fresh surface to action by the solution. If exudations of reaction product are not observed within two weeks, the aggregate is considered to be non-reactive. Again, all the Indiana aggregates subjected to the pat test failed to react.

Salts

The action of sodium and magnesium sulfate has long been utilized in a soundness test for aggregate and occasionally in concrete—a test the

Figure 3. A concrete core stored for six months in concentrated calcium chloride (after successfully withstanding 74 cycles of freezing and thawing).

author considers to be of doubtful value at best. These salts cause disintegration of concrete in two ways: by crystal growth with resulting pressure in pores and by a chemical reaction to convert calcium aluminate to calcium sulfoaluminate. Sodium chloride, often used as an ice-control chemical, can in sufficient concentration cause disruption of concrete by crystallization in pores, and can result in scaling of pavements. Calcium chloride, also used as an ice-control chemical, will not crystallize under normal outdoor humidity, but can in sufficient concentration cause disintegration of concrete by chemical action, presumably by conversion of calcium aluminate to calcium chloroaluminate, with resulting scaling. Figure 3 illustrates destructive action of concentrated calcium chloride on a concrete core which had previously withstood 74 cycles of freezing and thawing. Various salts can be leached from the soil, carried upward through a pavement by capillary action, and deposited as crystals in the surface pores of concrete. These crystals can cause disruption of the surface layer and can hasten the loosening of paint films. Attack by sea water is primarily by action of chloride and sulfate ions below water level and crystallization of salts above water level.

FIGURE 4. A cement mortar cube stored to half its depth in one normal calcium chloride for six months (with resultant evaporation and concentration of the salt in the top of the cube).

Studies of salt action can frequently be made by chemical analysis, following changes in concentration of salts in solution and changes in composition of mortar on concrete specimens. The microscope is a most valuable tool in such studies, and should be employed much more than it is. Figure 4 illustrates disruption of a mortar cube exposed to a salt-evaporation test. Physical tests involving wetting and drying, evaporation, etc., are applicable to such studies.

Acids

A few soils have a pH value sufficiently low to promote attack of the alkaline mortar (a powdered concrete slurry has an equilibrium pH of about 12). These soils usually have a high humus content. Many types of sewerage are highly acidic and attack concrete rapidly.

Chemical analysis and microscopic studies usually suffice to detect and analyze acid disintegration. Marked corrosion may be identified microscopically.

Solution by Water

In dams with a large head of water, this may be a serious problem, although concrete has a very low solubility. Rate of solubility depends

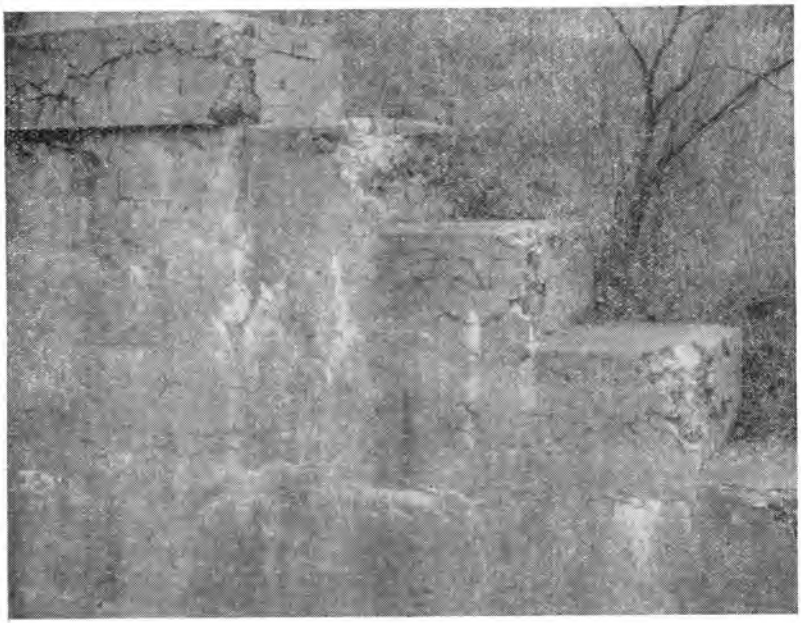

Figure 5. Concrete illustrating solubility and disintegration (white stains are primarily calcium carbonate dissolved from the concrete).

upon rate of renewal of solvent and thus increases as cracks and holes grow. It is possible that solvent action may increase pore space and thus aid disruption by freezing-and-thawing action. Ridges of calcium carbonate outlining cracks on pavements show that solution in these pavements is not inconsiderable. These ridges are usually dark in color from absorbed dirt, and are readily worn away by traffic. Figure 5 illustrates solvent action of water on concrete.

Chemical analysis of effluent water and undissolved concrete furnishes a base of study of solvent action.

Capillary Flow

Upon changes of temperature in wet concrete, water will tend to expand or contract and, if a differential in temperature exists, will tend to flow from the warmer to the cooler region. Rate of flow of water through fine capillaries is slow, and appreciable pressures may be generated if the temperature changes are rapid.

The microscope can be used to study pore structure—number of pores, size of pores, shape of pores, etc. Physical studies of specific

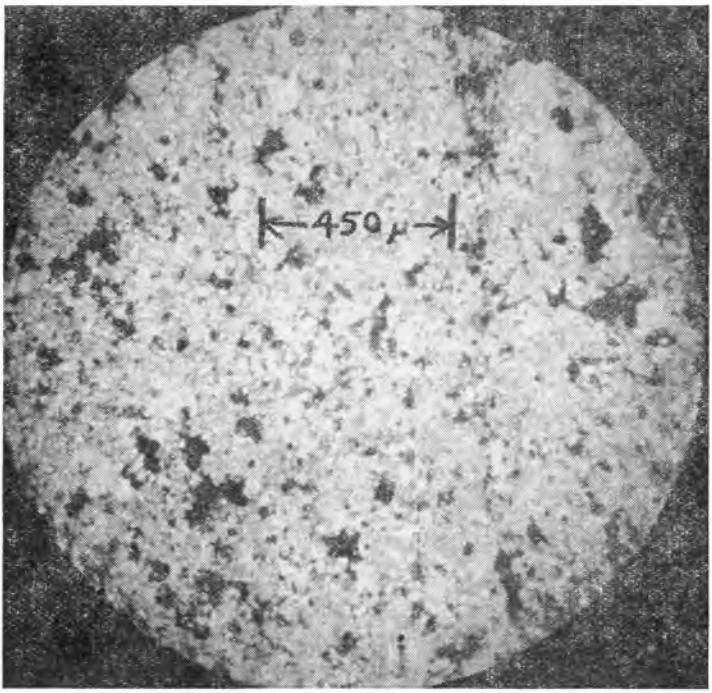

Figure 6. Photomicrograph of a porous limestone-crossed nicols.

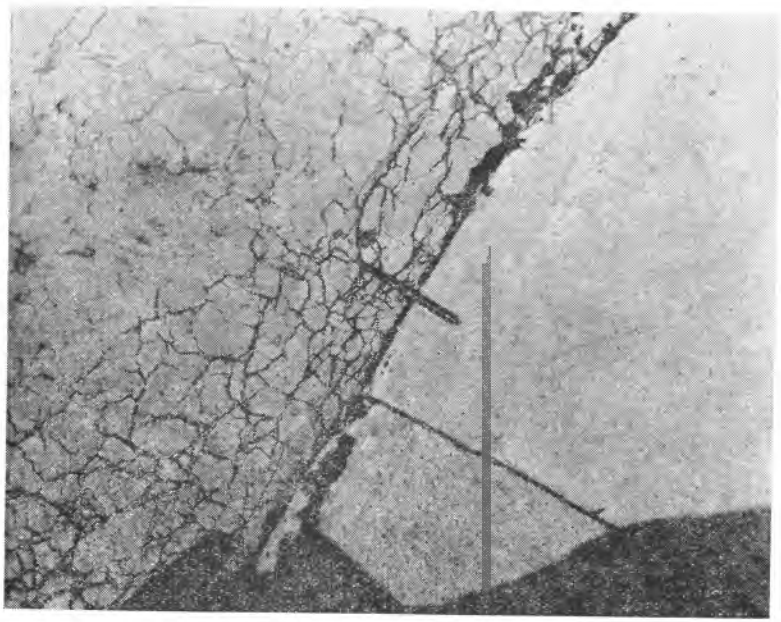

FIGURE 7. Disintegration of concrete presumably caused by freezing and thawing action.

gravities, rates of flow, and transmitted liquid pressures can be used in studies of capillarity. Figure 6 is a photomicrograph illustrating pore structure of a limestone. The black areas are holes.

FREEZING AND THAWING

Water expands about eleven percent in volume upon change from the liquid to the solid phase. The resulting pressure in a confined space—a pore in concrete or aggregate—is a crystal pressure analogous to that exerted by growth of salt crystals. Capillary pressure, as water is forced away from regions of crystallization, is also involved. Figure 7 shows mapcracking of a concrete runway, presumably caused by freezing and thawing of porous aggregate.

Studies of freezing and thawing have involved cycling of beams with measurement of changes in strength and modulus of elasticity, changes in length, and microscopic analysis of pore structure. Perhaps in the last method lies the greatest promise of advancement of knowledge of the problem.

In conclusion, a plea is made for increased use of physico-chemical techniques in research on concrete disintegration to supplement the

empirical methods now widely employed, and for better use of the technical literature already available.

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